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IMPROVED METHOD FOR SYNTHESIS OF DIFUNCTIONAL FLUOROALCOHOLS

BY DR. TIMOTHY J. JUHLKE, DR. THOMAS R. BIRSCHENK,
DR. HAJIMU KAWA, AND DR. RICHARD J. LAGOW
(EXFLUOR RESEARCH CORPORATION)

FOR NAVAL SURFACE WARFARE CENTER
RESEARCH AND TECHNOLOGY DEPARTMENT

3 JUNE 1991

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FOREWORD

The work described in this report was performed by Exfluor Research Corporation at their facility in Austin, Texas, under Contract N60921-89-C-0042 as part of the NAVSWC SBIR Program. The work was performed during Phase II of the overall effort. It is based on results obtained during the Phase I task which are summarized briefly.

The objective of the overall effort was to develop improved methods for the manufacture of fluorinated α,ω -alkanediols which are of interest as monomers for a variety of polymer applications, including binders for explosives.

Approved by:

W. Wayne Reed

WILLIAM H. BOHLI, Head
Energetic Materials Division



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INTRODUCTION

During the preceding Phase I SBIR research program, Exfluor Research Corp. demonstrated the feasibility of producing difunctional fluoroalcohols by direct fluorination of suitable alkane precursors. We used our fluorination technology to produce one pound each of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol, of 2,2,3,3,4,4,5,5-octafluoro-1,10-decanediol, and of 2,2,4,4,5,5,7,7-octafluoro-3,6-dioxaoctane-1,8-diol (octafluorotriethylene glycol). The phase I work was conducted on a fairly small scale with non-optimized conditions, but gave very good yields in the fluorination to the corresponding acid derivatives and their subsequent reduction to the appropriate diols. The purpose of the Phase II research was to determine how best to scale up the processes. To do so, a miniplant was built capable of producing five pounds per day of any one of the diols. In the process, information was gained that would be needed for further scale-up. During the Phase II program, we delivered over two hundred pounds of fluorinated diols produced during the scale-up process development.

FLUORINATION EQUIPMENT

To perform this research, we built a miniplant for the fluorination of hydrocarbon acid derivatives and a system for reducing the acids to diols. Two walk-in hoods were built, using concrete blocks to keep the costs down. Each hood has a depth of about 12 feet and a width of about 8 feet with a common 12-foot wall between them. The height of each wall is 8 feet. For a roof, we used a sandwich of fireproof sheetrock around 1/2-inch plywood installed in 2-foot sections using angle iron to support the panels. One 2-foot roof section in each hood was left open as an explosion door and to allow mounting a lift for the fluorination reactor. A single exhaust fan was used for both hoods. A crude drawing of the hoods is shown in Figure 1.

The fluorination reaction was done in a liquid phase fluorination reactor. A drawing of the reactor essentials is given in Figure 2. For this Phase II program, we decided to build a reactor with a flanged, removable top as that allows the reactor to be easily cleaned and inspected. To have the capacity needed for this study required a liquid volume of 5 to 6 gallons; therefore it was decided to build the overall reactor with a volume of about 10 gallons. The reactor is made of a 2-foot section of 12-inch schedule 40 aluminum pipe which has a flat bottom welded to it made of 1/2-inch aluminum plate. The top of the reactor is flanged with a 1/2-inch aluminum plate ring welded to the outside of the 12-inch pipe. The reactor top then bolts to this flange ring. The reactor top is made of 3/4-inch aluminum plate as it has some pieces for the rotating seal that are held to it by bolts. The feed throughs for the gas inlet line and the liquid return from the condenser to the reactor are pieces of 3/8-inch copper tubing that are fed through drilled out Swagelok male pipe threads to compression fittings. The top plate is threaded for these Swagelok fittings. The inlet line for the organic compound is run inside the liquid return line and is made of 1/16-inch stainless steel tubing. The metering pump for the organic feed is a Milton-Roy liquid chromatograph pump. The condenser is made of a 2-foot section of 6-inch aluminum pipe that is welded at the bottom and flanged at the top. The gas inlet and liquid return lines are at the bottom of the condenser. The gas exit is at the top of the condenser as are the feed throughs for the cooling coils. The cooling coils consist of 150 feet of

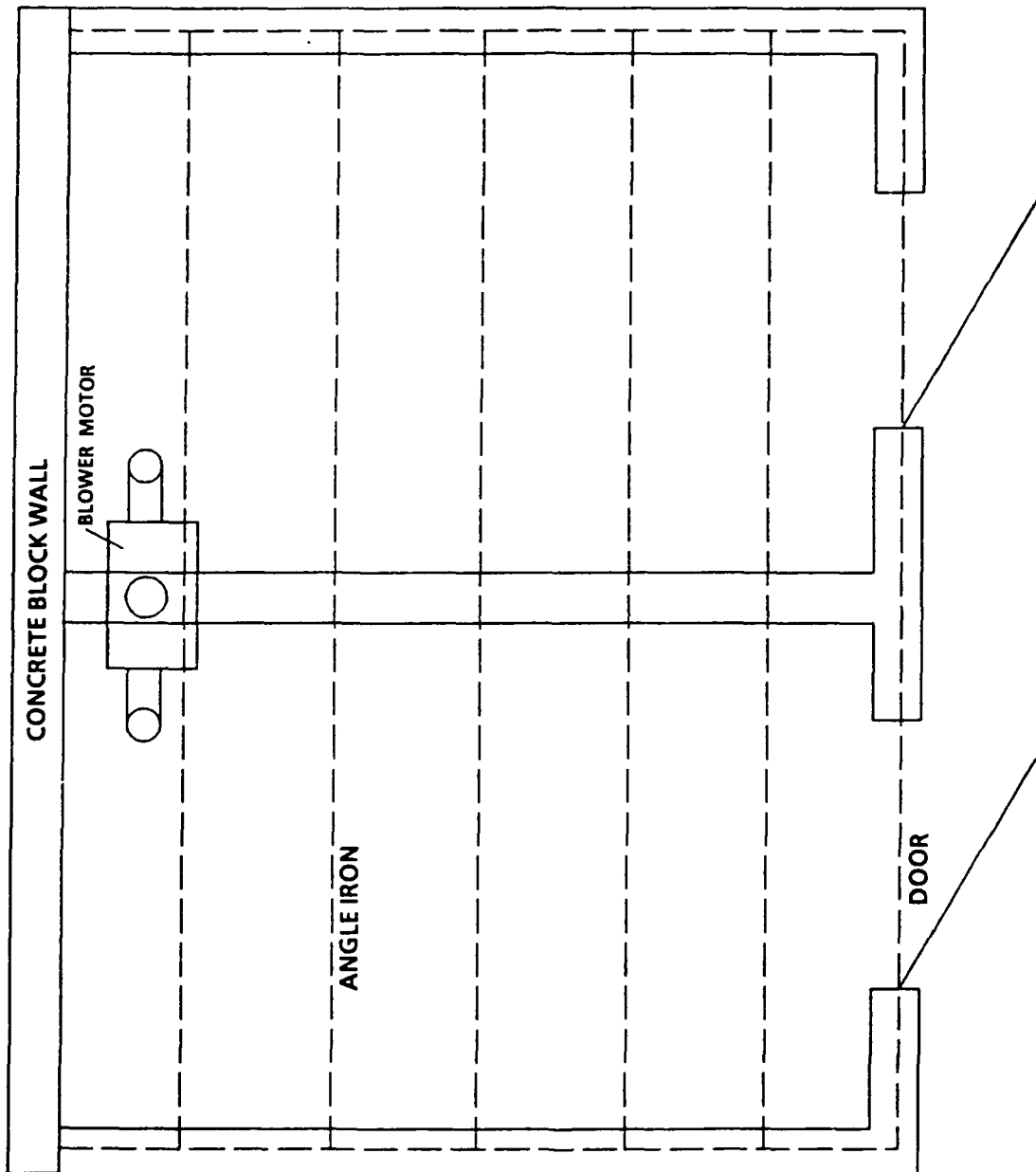


FIGURE 1. WALK-IN HOODS

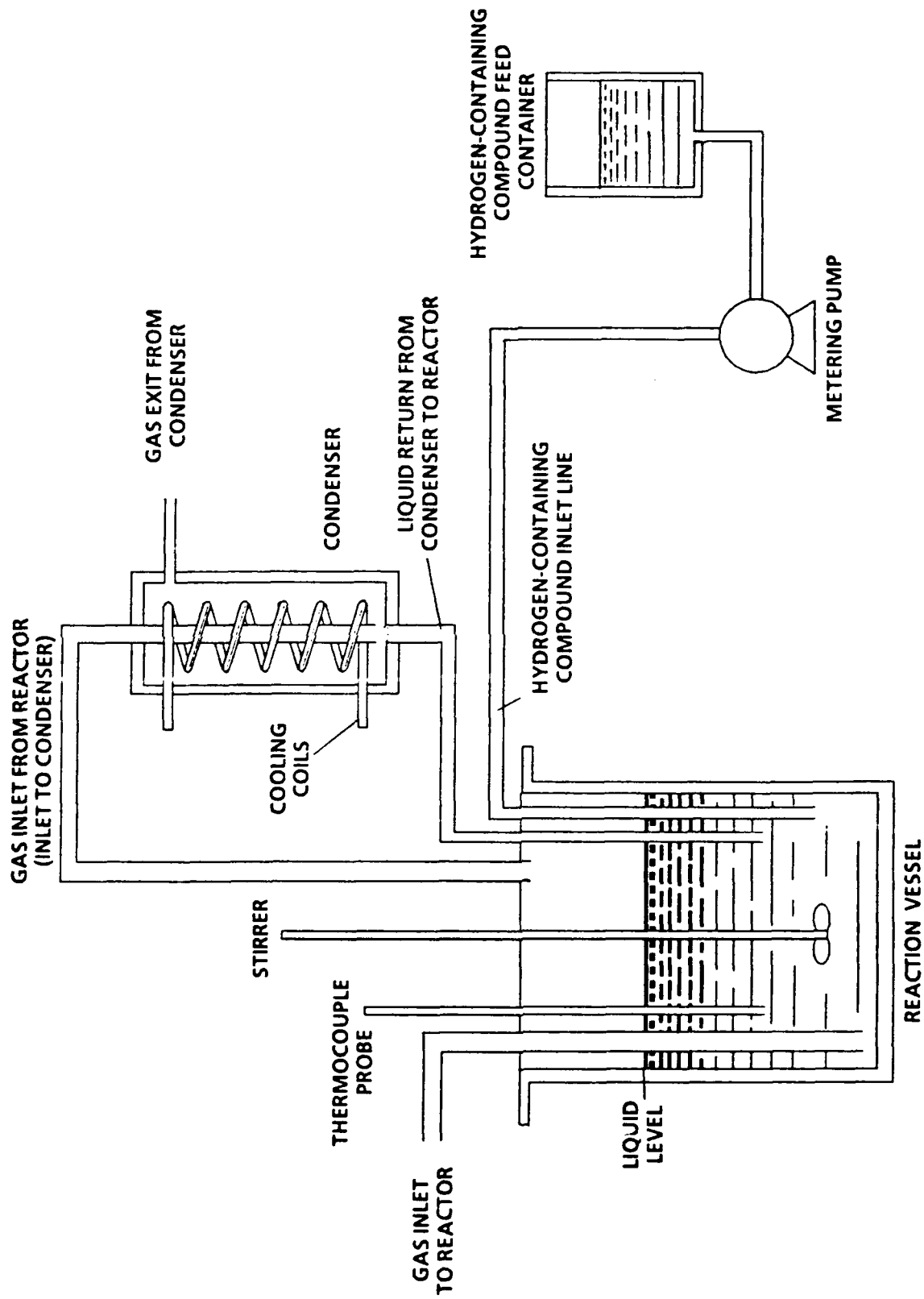


FIGURE 2. SCHEMATIC DRAWING OF REACTOR

3/8-inch copper tubing. A small 1/4 H.P. Freon 12 compressor is used to keep the cooling coils cold by using the cooling coils as the evaporator of a refrigeration unit. Once everything was assembled, the condenser was insulated. The reactor was run while placed in an ethylene glycol/water bath. This bath was cooled with a 3/4 H.P. Freon 12 refrigeration unit that utilizes 1/2-inch copper tubing placed in the bath as the evaporator. The temperature of the bath is controlled by a Honeywell thermostat whose sensor bulb is immersed in the bath. A small stirrer is used to keep the bath fluid uniform. The entire fluorination reactor is installed on a cart built from channel iron, unistrut, and angle iron. On this cart are mounted both refrigeration compressor units (for the condenser and for the bath), the bath for the reactor, and the condenser. The condenser is mounted with the bottom about 18 inches above the top of the reactor to allow liquid that condenses to flow back into the reactor. All of the connections for the gas inlet and the lines from the reactor to the condenser are 3/8-inch O.D. FEP Teflon tubing. This permits the reactor to be removed from the bath without being disconnected. This also allows visual inspection to make sure the liquid return line is not plugged.

The reactor is stirred with a 6-inch stainless steel propeller blade mounted on a 3-foot long by 1-inch stainless steel rod. The shaft is fed through the top plate of the reactor and sealed with a custom built rotating seal. The rotating seal is housed in an assembly that bolts to the top of the reactor. The actual rotating seals are spring-loaded graphite fiber-filled Teflon flange seals made by Bal Seal Engineering Co. One flange seal sits on top of the reactor and a second seal sits between the bearing housing and a 1-inch spacer that houses the two rotating seals. The bearing housing is 12 inches long and holds two sets of ball bearings about 10 inches apart to hold the shaft stationary and prevent wobble. The bearing housing and the spacer that houses the flange seals bolt directly to the center of the top plate of the reactor. After polishing with fine sandpaper, the shaft fit through this assembly into the reactor. There is also a gas inlet into the center of the spacer that houses the two spring loaded flange rotary seals. By feeding nitrogen through this gas inlet, all of the fluorine and other gases can be kept from the ball bearings. This mechanical rotating seal has worked very well for us. During our first run with this reactor, we had some difficulties with the expansion valve on the refrigeration unit that cools the condenser. This caused evaporation of the liquid and the liquid level in the reactor during the first run to get very low. This allowed the shaft to "walk" and quickly destroy the bottom rotating seal between the reactor top and the spacer. However, the top seal did not leak as it is installed very close to the ball bearing that holds the shaft in place. Because this top seal did not leak, neither seal was replaced.

Nearly 2 years later, the top seal still does not leak and the original rotating seals are still being used. When running the reactor, we keep about 500 mL/min. nitrogen flow on the seals, which then enters the reactor as a diluent gas. The shaft is driven using a Dayton 1 H.P. 90V DC motor that is mounted on a frame made from angle iron bolted to the top of the reactor. The motor is coupled to the shaft using a spider coupling. The motor is then plugged into an outlet of the motor control unit that is installed on the reactor cart. In a typical run, the reactor is stirred at about 1000 RPM. In general, the more agitation, the better the reaction proceeds.

Inside the reactor were placed baffles made of 1-1/2-inch by 1/8-inch aluminum plate. Two pieces of this plate run up the sides of the reactor to about 6 inches from the top and a third piece of plate is bolted to the bottom of each side baffle and is wedged into the reactor as it is bolted, since it has a slightly larger dimension than the inside diameter of the reactor. By using removable baffles, we were able to experiment with different kinds of baffles.

The gases used in the reaction are nitrogen and fluorine. It was decided to use a low pressure manifold using only 2 fluorine cylinders even though at the higher flow rate a cylinder of fluorine is consumed in less than 8 hours. In this way, we were not tempted to leave the reactor uninspected for too long a period of time. The fluorine was metered using a 0 to 10 L/min. stainless steel mass flow controller made by MKS Instruments that has an all-stainless steel control valve (the SP-052 option). The nitrogen was metered using the same controller with the regular control valve. The nitrogen and fluorine are mixed by combining the 2 streams in a Swagelok tee. Some nitrogen flow is maintained at all times to prevent air from getting into the fluorine controller. The nitrogen pressure is always maintained at a level significantly higher than the fluorine pressure; thus, if an obstruction develops in the system, the fluorine flow will be shut off first. In general, we keep the nitrogen pressure at 20 psig. The fluorine pressure will vary from about 5 psig to 10 psig as the cylinders are emptied. All fluorine regulators are single stage regulators and their delivered pressures increase as the cylinder pressure decreases. This fact permits the use of just 2 regulators and 2 cylinders, as the fluorine will always flow from the cylinder with lower pressure if the regulators are set at the same level. Therefore, one cylinder is emptied completely before the fluorine in the other cylinder begins to flow. In our system, the fluorine cylinders were positioned inside the hood with the reactor, but the flow controllers, shut-off valves, and electrical kill switches were mounted outside the hood by running tubing through the concrete block walls. A pressure sensor at the reactor inlet line is used to check the system for obstructions.

The off-gases from the reactor, which include excess fluorine and hydrogen fluoride, were scrubbed with aluminum oxide pellets. Both hydrogen fluoride and fluorine react very efficiently with aluminum oxide to produce aluminum fluoride. Aluminum fluoride is classified as a nonhazardous material and is also a by-product of aluminum manufacture. The aluminum oxide scrubber permits the use of an oxygen meter for the exit gas from the scrubbers to monitor the amount of fluorine coming out of the reactor, as each mole of fluorine will liberate 1/2 mole of oxygen. For our scrubber system, we used a primary alumina trap, a water trap, and a backup alumina trap. The primary alumina trap is made from a 4-foot section of schedule 40 mild steel 4-inch pipe (Figure 3). One end of the pipe is flanged with 1/4-inch steel plate and the other end is threaded. The flanged end is used as the top of the trap and the threaded end is capped with a cast iron cap. The cast iron cap is drilled out and threaded to hold a male 1/4-inch Swagelok pipe fitting. This fitting is placed on the side at the bottom of the cap so the trap can rest on the cast iron cap. A section of stainless steel tubing with 1/4-inch pipe thread at one end and 3/8-inch compression fitting at the other is used as the gas exit for the alumina trap. A 1/4-inch steel plate fitted with a gas inlet in the same fashion as described for the bottom cap is used as the top of the trap. For best efficiency, the gas inlet must be at the top of the alumina trap and the exit at the bottom. The trap should also be installed vertically. The bottom compression fitting is the only part that has shown significant wear during the course of this contract effort. It required replacement about every 3 months as it slowly eroded away. To fill the alumina trap, a small amount of stainless steel turnings obtained from a Chore Boy stainless steel scouring pad is wedged into the Swagelok fitting before the 1/8-inch or 1/4-inch aluminum oxide pellets are put into the trap. After this first alumina trap, we placed a water trap to catch most of the water resulting from reaction of aluminum oxide with hydrogen fluoride. For a water trap, we used a 1-gallon plastic bottle into which FEP tubing is fed through holes cut into the top. The water trap is followed by a second alumina trap made from a 3-foot section of 2-inch mild steel pipe. If a temperature rise is detected in this second or backup alumina trap, the first alumina trap should be replaced.

All of the plugs that developed in the system were found at the bottom of the first alumina trap. During a typical fluorination run, about one in every two or three primary alumina traps will slowly start to form a plug causing the reactor pressure to rise. This usually occurs when the trap is about 2/3 used up. During the first 1/2 of the capacity of the alumina trap, all of the water formed from the reaction of hydrogen fluoride with aluminum oxide is absorbed by the unused

* A Sensormedics OM14 Oxygen Analyzer was used.

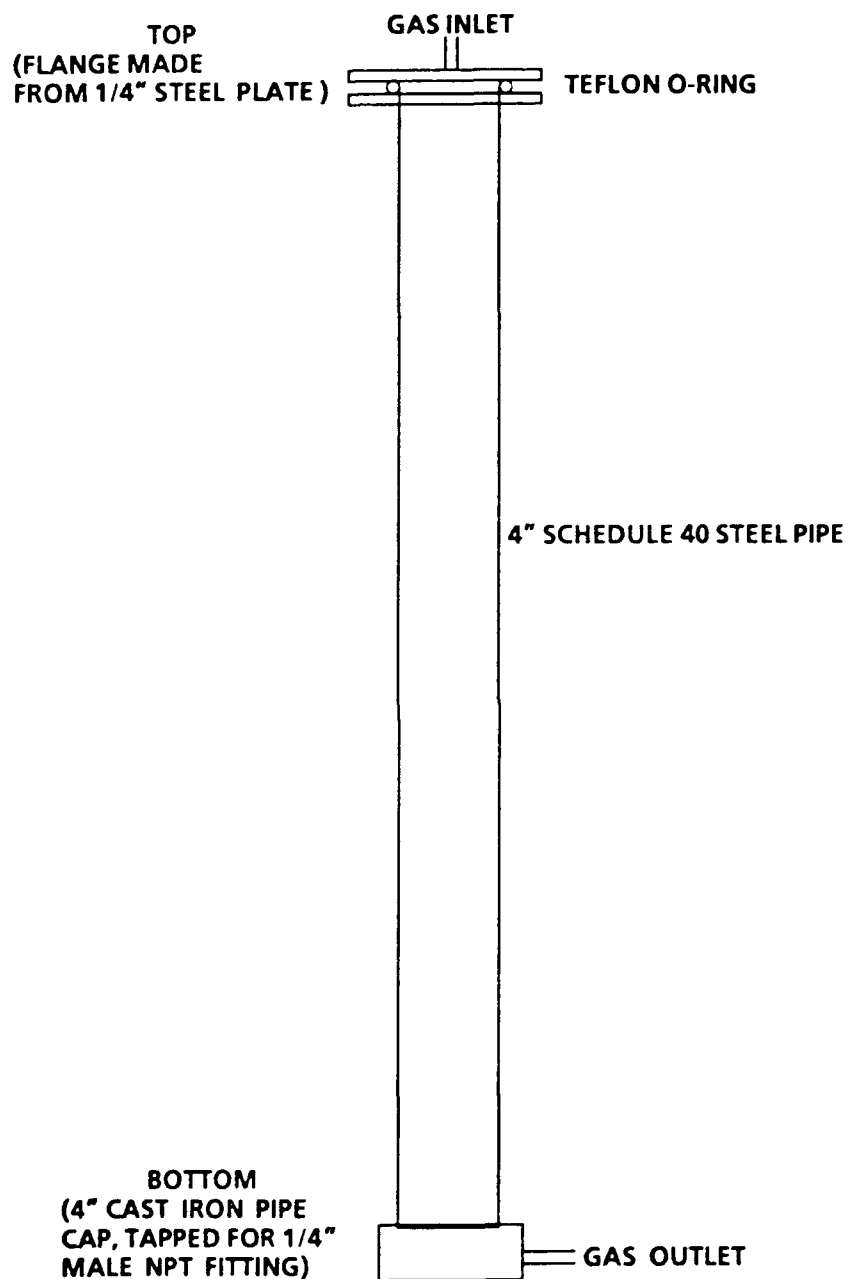


FIGURE 3. PRIMARY ALUMINA TRAP

aluminum oxide in the bottom of the trap. Subsequently, most of the water collects in the water trap. Plugging can be prevented easily as follows: when water starts to come over into the water trap, the trap is disconnected and a nail is driven through the fitting at the bottom of the primary alumina trap. When the nail is removed, the exit line is opened. The pellets at this stage are reasonably well agglomerated by the action of the water and other materials so that no solids will drop out of the bottom fitting. When this preventive procedure was followed, no further plugging occurred.

GENERAL FLUORINATION PROCEDURE

For a typical reaction in the reactor described in the previous section, 5 to 7 gallons of a solvent that is inert to fluorine under the reaction conditions is placed in the reactor, the reactor is purged with nitrogen, and the condenser is cooled. Fluorine is diluted with nitrogen and introduced into the reactor through the gas inlet. The organic feed is then started using the metering pump. The flows of fluorine and organic feed are balanced so that about 5 percent excess fluorine is used. An oxygen meter placed after the alumina traps can be used to make certain that the feed rates are balanced. The reaction is then run until all of the organic material is pumped in. At the end of the reaction, the organic feed pump is turned off as is the fluorine flow. The reactor is then purged with nitrogen and it can then be dumped. Allowing the reactor to sit with a nominal flow of fluorine and nitrogen for 15 to 30 minutes before turning off the fluorine and purging with nitrogen sometimes helps insure that the product is completely fluorinated.

The amount of nitrogen diluent gas used depends in large part on the specific system. This will be discussed in more detail for each compound later. However, in general, enough nitrogen is needed to stay below the flammable limits of the solvent. With Freon 113, this is generally about 30 to 40 percent of fluorine, depending upon the temperature and other factors. For some solvents such as 3M's FC-75 (mostly perfluorobutyltetrahydrofuran) it is lower than 20 percent fluorine. As long as flammable limits are not exceeded and there are no hot spots, the solvent will not react with fluorine.

The perfluorinated diacids made in this study were converted to the methyl esters as described later for the individual products, because the methyl esters can be reduced easily to alcohols with little or no aldehyde formation. The methyl esters are also stable liquids that can be distilled and easily handled. The diacids are solids that are more difficult to work with. Consequently, the crude perfluorinated esters were reacted with methanol in the reactor after the fluorination and before the product was dumped and worked up.

During the Phase II program, large scale runs were made with both acetate esters of hydrocarbon diols and methyl esters of

hydrocarbon diacids. After the fluorination was complete, the products were reacted with methanol in the reactor with evolution of hydrogen fluoride. Methanol reacts with the perfluorinated esters to give the methyl esters of the perfluorinated acids. Dimethyl carbonate was a by-product when methyl esters of diacids were used as starting materials, and methyl trifluoroacetate was the by-product when acetate esters of diols were starting materials. Some of the hydrogen fluoride produced during the methanolysis remained with the excess methanol and was also present in the crude product dumped from the reactor. Because of the presence of hydrogen fluoride, a small metal still was built to remove it, the solvent, methanol, and by-products from the desired dimethyl esters. A glass still would not last long because of the hydrogen fluoride present.

This small still (Figure 4) was made from a 15-inch length of schedule 40 8-inch diameter stainless steel pipe. This pipe had a welded bottom and a flanged top. To the flanged top was connected a 1-inch schedule 40 carbon steel nipple that connected to a coupling leading to the condenser. A small flow of nitrogen was introduced through a tube fed through the top plate to the bottom of the still to prevent bumping. For a condenser we used a 2-foot length of 3-inch schedule 40 carbon steel pipe with threaded ends. For cooling coils, we used 50 feet of 3/8-inch copper tubing which was used as the evaporator of a Freon 12 compressor unit. By using a programmable temperature controller and a thermocouple in the still bottom, the distillation could be done without operator attention other than during loading of the still and changing of the receivers for the different temperature ranges. The receivers used were 5-gallon plastic pails that were fed by a 1/4-inch FEP tube attached to the bottom of the condenser.

Methyl trifluoroacetate, methanol, and Freon 113 have boiling points too close for good separation by distillation. For runs made with acetate esters of diols, the material that distilled below a still bottom temperature of 160°C was combined, washed with water to removed methanol and then with aqueous sodium hydroxide to remove the methyl trifluoroacetate. The remaining Freon 113 was dried with magnesium sulfate or potassium carbonate and reused in fluorinations. For runs with the methyl esters of diacids, the Freon 113 was removed by distilling to a still bottom temperature of about 85 to 90°C which was held for about 30 minutes. This fraction contained all of the Freon 113, some methanol and some dimethyl carbonate. This mixture was washed with water, then with aqueous sodium hydroxide, and dried to give Freon 113 that could be reused. Subsequently the temperature was raised to about 10 degrees below the boiling point of the desired product and held for several hours to remove all of the dimethyl carbonate and methanolic hydrogen fluoride. At this stage, the product could be distilled further in glass without significant etching.

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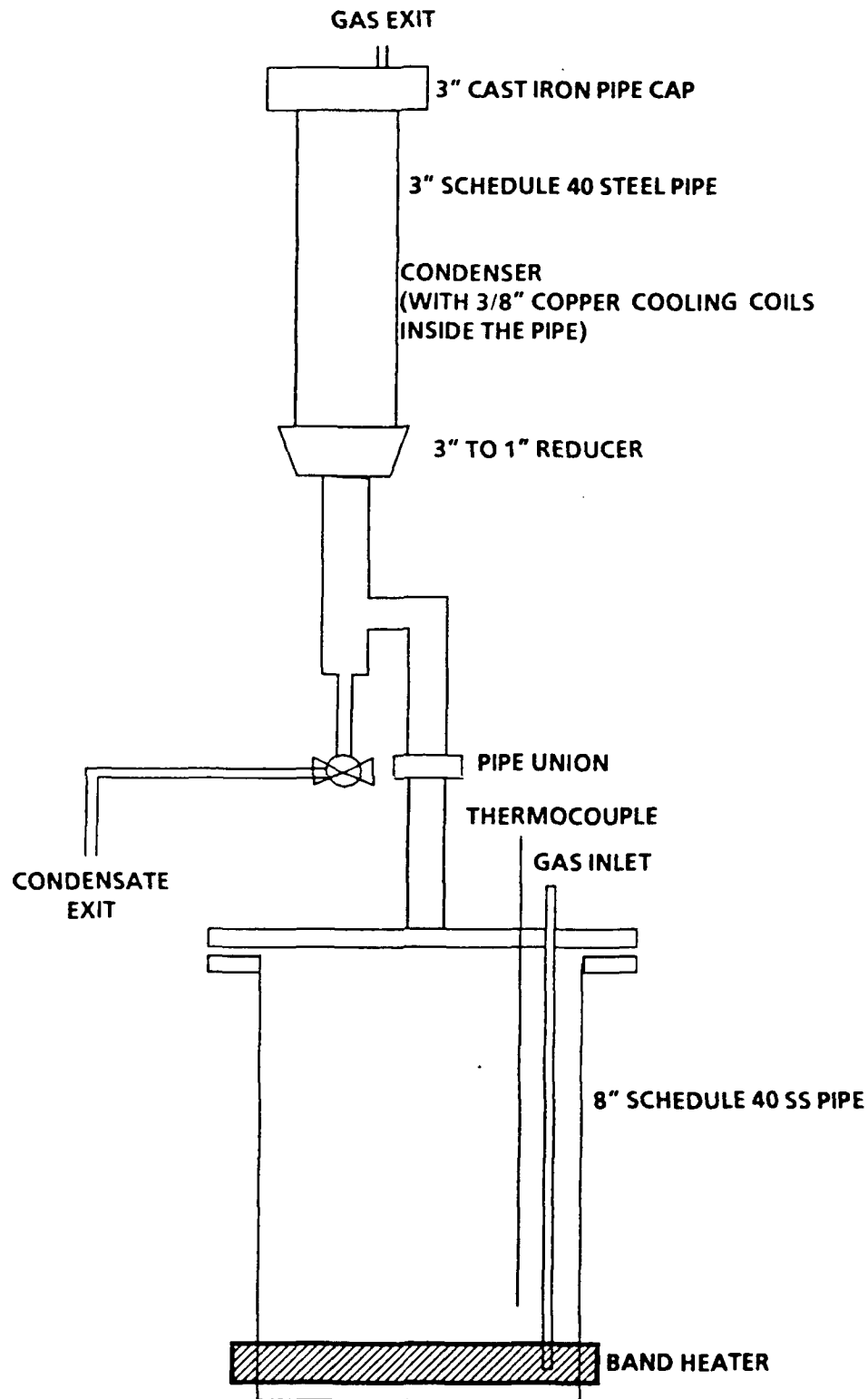


FIGURE 4. METAL DISTILLATION APPARATUS

REDUCTION APPARATUS

A small apparatus was built for the larger scale reductions (Figure 5). The body of the reactor was made of a 2-foot length of schedule 40 8-inch aluminum pipe with flanged ends. For the bottom, we used a 1/2-inch aluminum plate bolted on as a blind flange. For the top we used a piece of polycarbonate so that the reaction could be observed visually. Through the top were fed a thermocouple, a liquid inlet, and a gas outlet line. In addition, a 6-inch nipple of aluminum schedule 40 1-inch pipe exited from the top. To the outside end of the nipple was attached a Swagelok quick connect which was used as a rotating seal for a length of 1/4-inch stainless steel rod that was used as the stirrer shaft. On the stirrer shaft were placed 2 small 5-inch aluminum fan blades to stir the reactor. A bubbler was connected to the gas outlet. A small nitrogen purge fed through the bubbler via a T was used to monitor the amount of gases being generated. The stirrer shaft was turned by a Milwaukee variable speed drill that was mounted on a frame made of angle iron bolted to the top flange of the reactor to hold it in place. The reactor bottom was immersed in a water bath of a laboratory water chiller/heater during the reaction. A Tracor Model 3000 liquid chromatograph pump was used as a dropping funnel as it has a very wide range of possible flow rates.

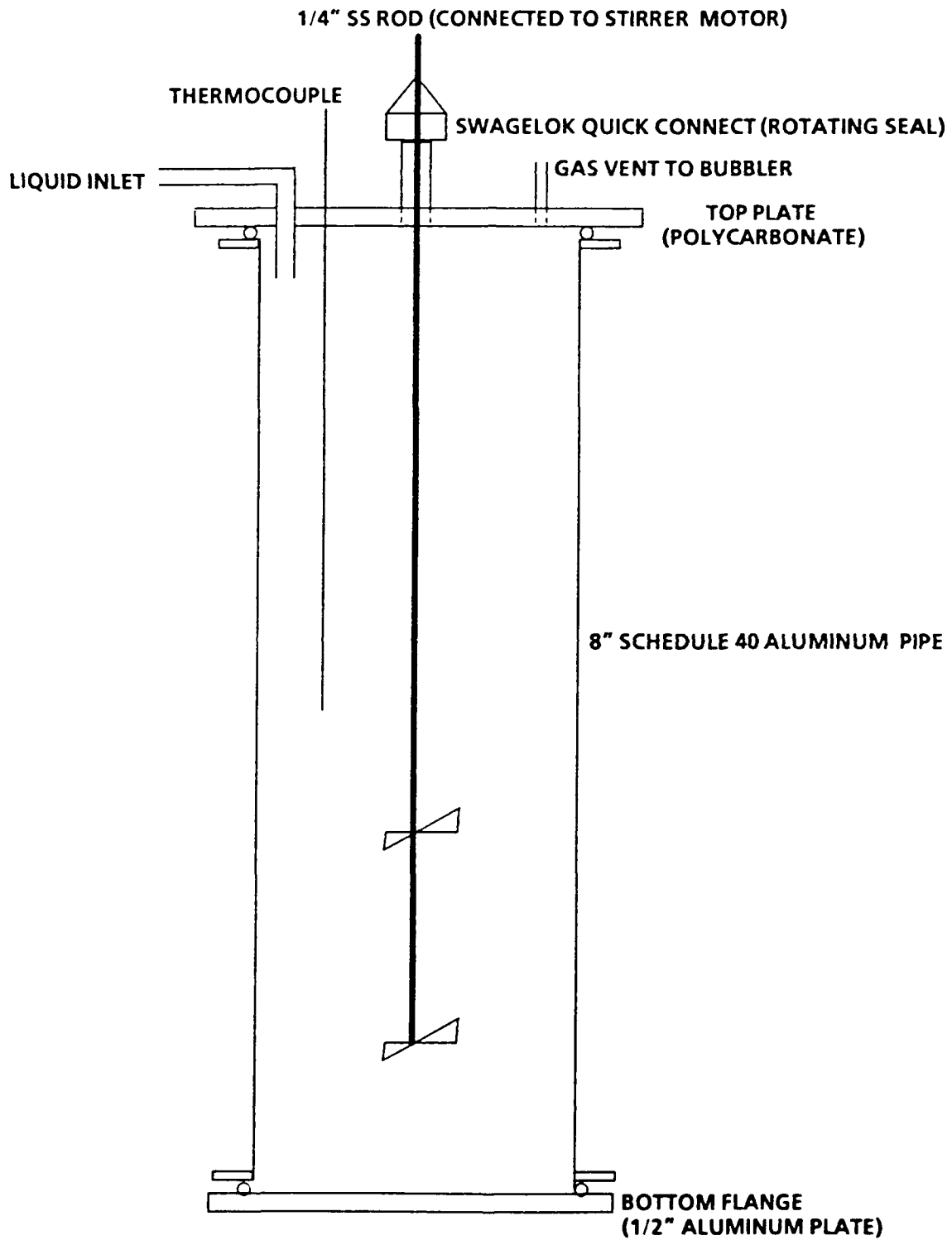


FIGURE 5. REDUCTION APPARATUS

GENERAL REDUCTION PROCEDURE

During the Phase I program, lithium aluminum hydride in tetrahydrofuran was used for all of the reductions. In Phase II a procedure was developed using cheaper materials that would also be safer to work with. This procedure uses sodium borohydride in isopropanol solvent. Although hygroscopic, sodium borohydride is reasonably stable to water and is much easier to work with than lithium aluminum hydride. Isopropanol is also much cheaper than tetrahydrofuran.

To carry out the reduction, 10 liters of isopropanol and a 25 to 50 percent excess of sodium borohydride (12.5 to 15 moles) are placed in the reactor which is then assembled and placed in an ice-water bath. Ten moles of perfluorinated acid dimethyl ester is added as rapidly as possible while keeping the reaction temperature below 35°C. In general, this will take about 90 minutes. After all the diacid has been added, the bath temperature is raised to heat the reactor above 40°C for at least 30 minutes. At this stage, the product is a somewhat viscous liquid. The reactor is cooled, and at about 30°C, a saturated aqueous ammonium chloride solution is added. This results in evolution of hydrogen. After about 1600 mL of the ammonium chloride solution is added, a mild exotherm occurs and hydrogen evolution is very rapid. Best results are obtained when about 1800 to 2000 mL of saturated aqueous ammonium chloride are added. This amount can vary somewhat, but when enough has been added, solids will precipitate from solution and hydrogen evolution will cease. If a larger excess of ammonium chloride is added, the water/isopropanol mixture will dissolve more of the solids which can make distillation or sublimation of the product more difficult.

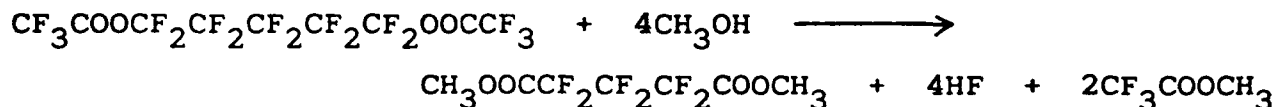
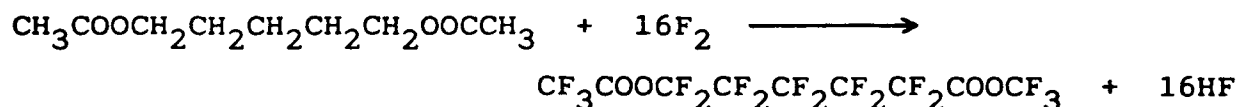
At this stage, the reactor is dumped and the product filtered from the insoluble solids. For this, a pressure filter, made from a 2-foot length of 1/8-inch aluminum pipe that is flanged at both ends, was used. The bottom flange has a short nipple of aluminum pipe attached to it. Two pieces of plastic window screen, cut to a smaller diameter than the Teflon O-ring in the flange, are placed between the bottom flange plate and a piece of filter paper with a diameter larger than the Teflon O-ring. This assembly is then bolted to the bottom flange of the pressure filter. The top flange plate has a valve attached to it by pipe threads. The

whole assembly fits on a plastic 5-gallon pail with a hole cut in the lid for the nipple to fit through. In general, 50 to 60 psig air pressure is used to force the liquid through the filter.

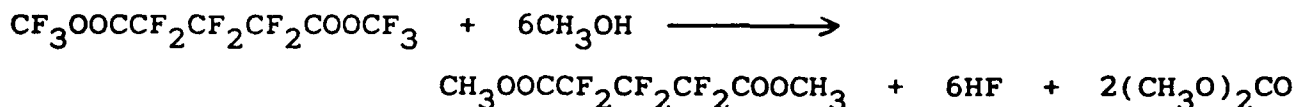
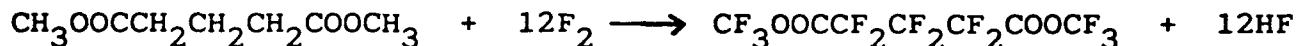
After the solution has been filtered, the isopropanol and water are distilled off from the product using a 12-liter flask. If the product tends to bump during this distillation, a small amount of water is added to the distillation flask. Other attempts to stop the bumping were unsuccessful, and the bumping has been severe enough to break a 12-liter flask filled with product. The bulk of the isopropanol and water are distilled from the product to a bath temperature of about 150°C to give a residual material that still contains a small amount of water, isopropanol, and some solids that were dissolved in the isopropanol/water mixture. Most of these solids can be separated by pouring the product hot (80°C) through a glass funnel lined with aluminum window screen. These solids are washed with dry isopropanol to recover any adhering product. At this stage, the product can be distilled or sublimed.

PRODUCTION OF 2,2,3,3,4,4-HEXAFLUORO-1,5-PENTANEDIOL

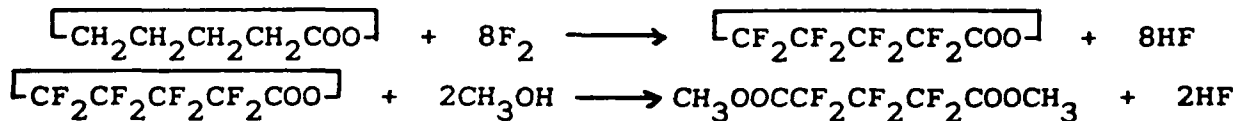
During the Phase I program, the diacetate of pentanediol was used to produce the diacid precursor for hexafluoropentanediol. As can be seen from the following equations, much of the fluorine used in the reaction does not end up in the final product. Because fluorine is the most expensive component of the reaction,



it is desirable to use a starting material that retains a higher percentage of fluorine in the product. This was accomplished by fluorinating dimethyl glutarate which requires only 75 percent of the fluorine of pentanediol diacetate. Du Pont makes dimethyl



glutarate and sells it for less than a dollar a pound in bulk under the name DBE-5. An even better source would be δ -valerolactone which would use even less fluorine as shown in the following equation. Unfortunately, we were unable to find a good source of δ -valerolactone. In addition, the fluorination of a C_5



compound would require a lower temperature condenser and a change of solvent as the perfluorinated material would be too volatile for the existing apparatus. We therefore decided that the best starting material was dimethyl glutarate.

The fluorination of dimethyl glutarate presents a few problems of its own. As the perfluorinated C_7 ester should be quite volatile, it is desirable to use a minimum of nitrogen during the fluorination. In addition, steric hindrance at the central carbon due to the two ester groups makes perfluorination more difficult than with a longer chain material. Another factor to be considered is how long to run the reaction. Because the workup involves most of the labor, it is desirable to run the reaction until as much product as practical is in the reactor. However, there is some indication that a small amount of product is lost due to extended exposure to the fluorination conditions. This is not surprising as perfluoroesters decarboxylate quite rapidly when treated with fluorine at about $100^{\circ}C$. Due to problems in fluorinating the central carbon in dimethyl glutarate, a reaction temperature of $30^{\circ}C$ was needed to consistently produce a perfluorinated product. At lower temperatures, significant amounts of mono- and dihydro-species were observed. The best fluorination conditions are determined by balancing all of these factors to arrive at an acceptable compromise.

In a typical run, the reactor was loaded with 6 gallons of Freon 113 and the reactor temperature was set at $30^{\circ}C$. With a fluorine flow rate of 2 L/min and the nitrogen flow set at 3 L/min (2.5 L/min mixed with fluorine and 0.5 L/min through the rotating seal), the dimethyl glutarate was pumped in neat at a rate that maintained an oxygen reading at the exit of the alumina traps between 1 and 1.5 percent. Response to changes in flow rates is sluggish due to the relatively slow reaction at the central carbon. These conditions are maintained for between 100 and 120 hours at which point the organic feed is stopped, the pump is rinsed with Freon 113, and the fluorine flow is reduced to 200 mL/min with a nitrogen flow of 1 L/min (1/2 mixed with the fluorine, 1/2 run through the rotating seal). These conditions are maintained until the oxygen reading remains steady. This usually takes several hours due to the difficulty in replacing hydrogen on the central carbon. At this time, the fluorine is turned off and the reactor is purged with nitrogen. The reaction is not run longer because the amount of methanol to be added would then more than fill the reactor. Ten to 20 percent over the theoretical amount of methanol is then pumped into the reactor while stirring is maintained and the nitrogen flow is maintained at about 3 L/min to sweep out the hydrogen fluoride. During the whole reaction, the condenser is kept at about $-30^{\circ}C$ to $-35^{\circ}C$. After the methanol has been added, the reactor is dumped and the product is transferred to the metal still. The Freon 113 is distilled off for 30 minutes to a still bottom temperature of

between 85 and 90°C. The rest of the dimethyl carbonate and other by-products are removed by heating the still to a temperature of 160 to 170°C and holding the temperature for about 8 hours. In a typical run, 9 to 10 kg of dimethyl glutarate are reacted and 12 to 13 kg of crude dimethyl hexafluoroglutarate are recovered. At this stage, the product is filtered and can be purified further by distillation. Typical yields of this crude product ranged from 80 to 82 percent. A gas chromatogram of the product indicated it to be quite pure but it usually contains a few percent of a dimer. The amount of dimer depends on how well balanced the flows are during the fluorination.

It was this crude product that was reduced to the hexafluoropentanediol. As there was little difference in the results when distilled product was used in the reduction, the distillation step was deemed unnecessary. The reduction of dimethyl hexafluoroglutarate requires a large excess of sodium borohydride because the dimethyl hexafluoroglutarate catalyzes the reaction of isopropanol or maybe methanol with sodium borohydride. Both distilled and crude dimethyl hexafluoroglutarate give the same result. About a 50 percent excess of sodium borohydride is needed for the reduction. Otherwise, the conditions used are given in the general reduction procedure outlined earlier. In a typical reaction, the yield of diol after sublimation is between 90 and 92 percent.

For the purification of the hexafluoropentanediol, sublimation was chosen as a simple process that required little operator attention. To obtain adequate purity, the product was resublimed as a small amount of tars and solids were entrapped in the product in the first sublimation. The sublimation apparatus used was built from 8-inch schedule 40 aluminum pipe (Figure 6). The bottom of the sublimator is a 15-inch length of this pipe with a flat welded bottom and a flanged top. This fits inside an oven made specifically to fit the 8-inch pipe. The top section is a 2-foot length of the 8-inch pipe that is flanged at both ends. One end is connected to the sublimator bottom with a Teflon O-ring between the flanges. This O-ring keeps the top section which is exposed to air much cooler than the bottom. A piece of 1/2-inch aluminum plate with provisions for a vacuum take-off is used to cap the top. This apparatus is evacuated with a two-stage vacuum pump protected by a liquid nitrogen trap to condense water and isopropanol. The base is then inserted into the oven and heated. The hexafluoropentanediol collects on the walls of the 2-foot piece of pipe that makes up the top section. To remove the product, the apparatus is cooled, disassembled, and the product is scraped from the top section. One can easily sublime 10 pounds of hexafluoropentanediol per day in this apparatus once the appropriate oven temperature setting has been determined by trial and error. A total of 80 pounds of hexafluoropentanediol was produced. A ^{19}F NMR spectrum of the twice-sublimed product is shown in Figure 7.

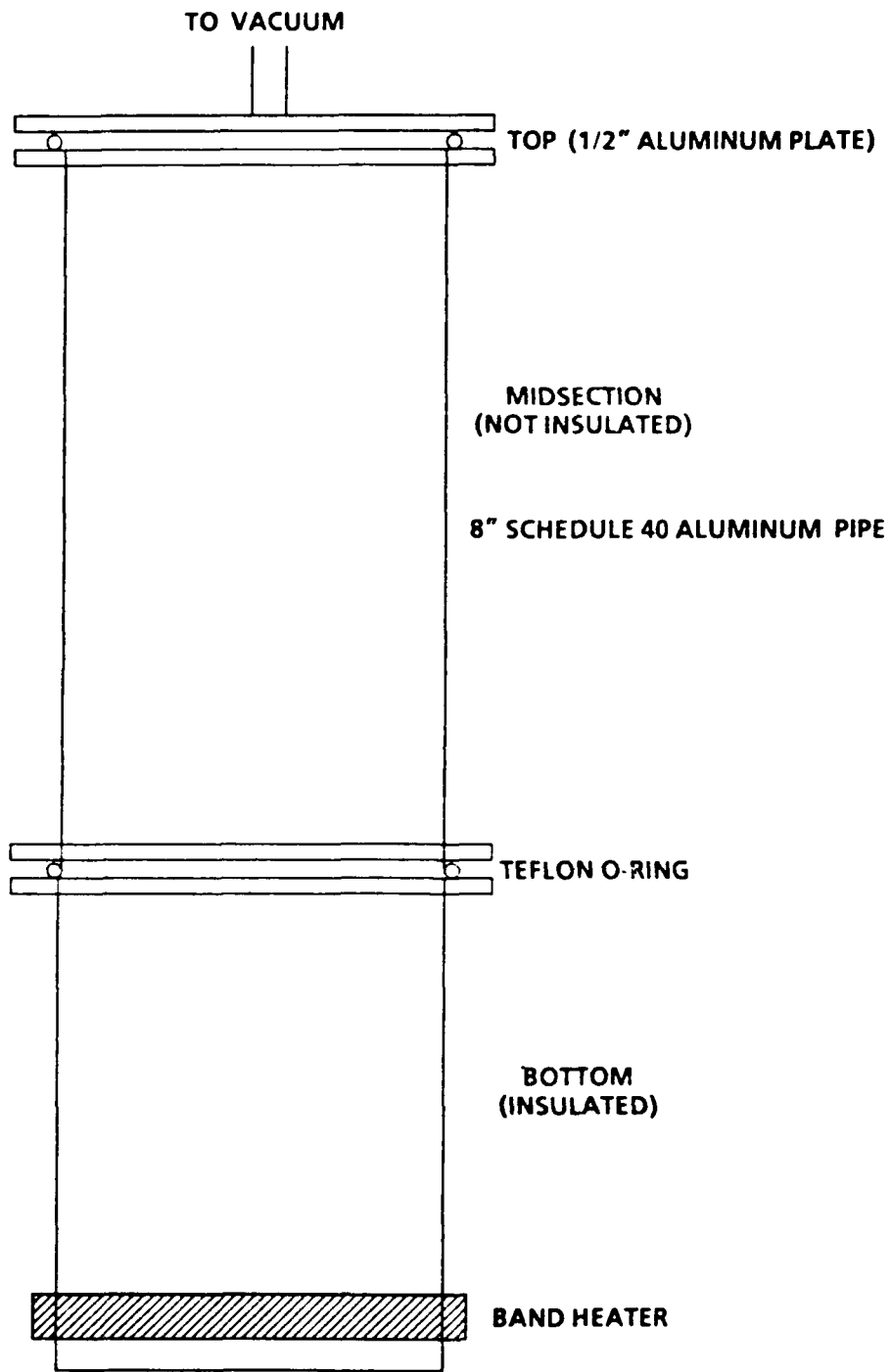


FIGURE 6. SUBLIMATION APPARATUS

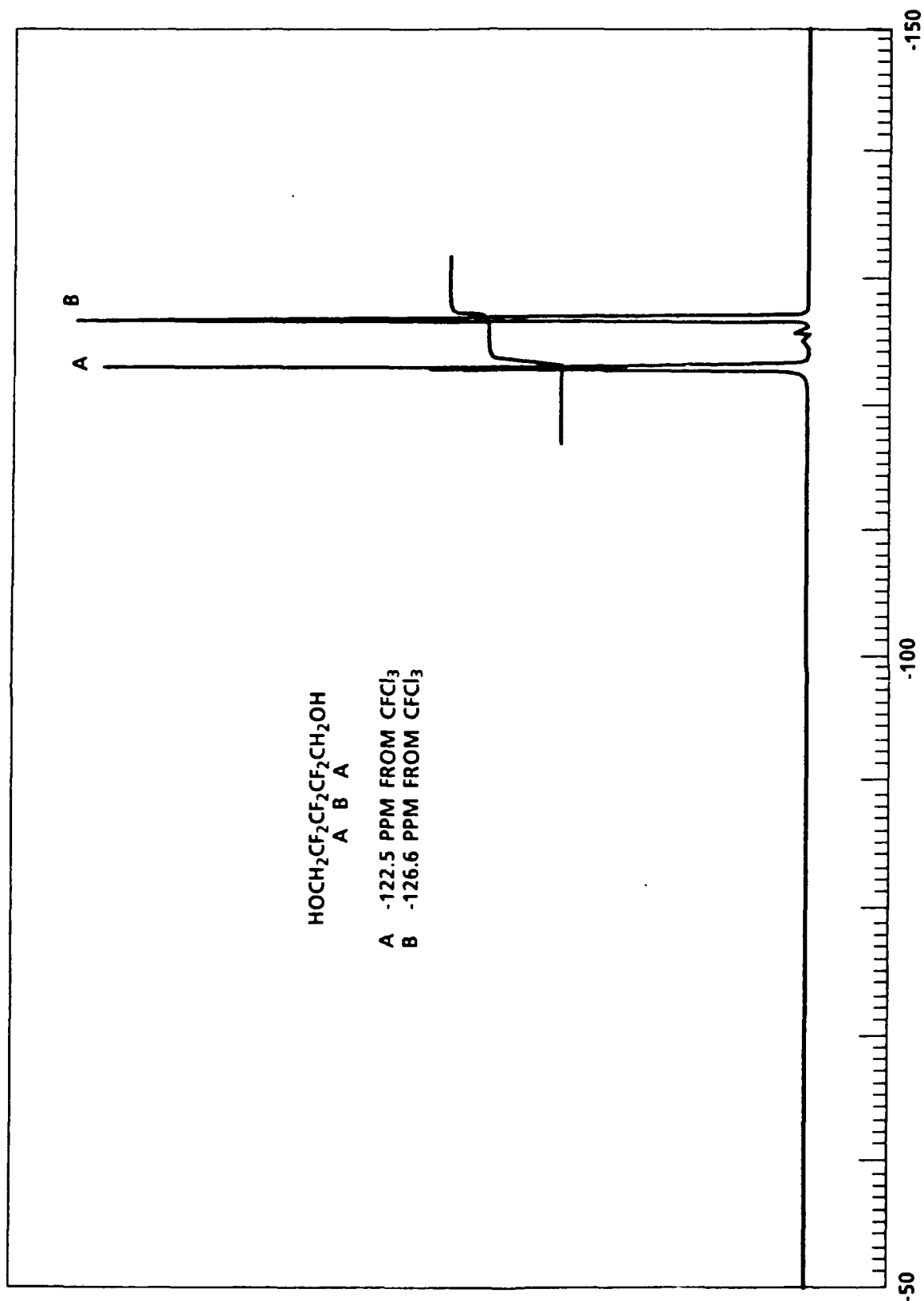
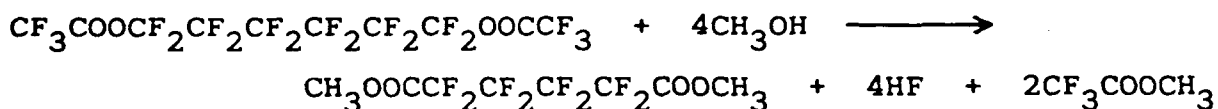
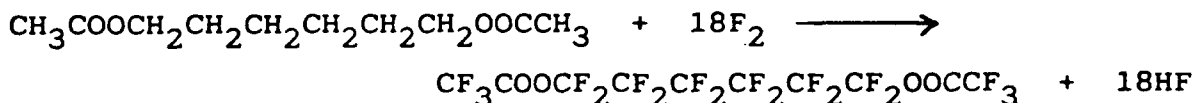


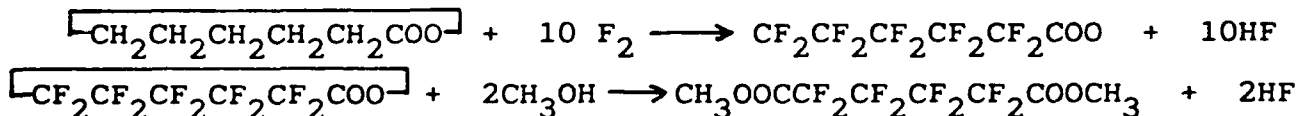
FIGURE 7. NMR SPECTRUM OF 2,2,3,3,4,4,4-HEXAFLUOROPENTANE-1,5-DIOL

PRODUCTION OF 2,2,3,3,4,4,5,5-OCTAFLUORO-1,6-HEXANEDIOL

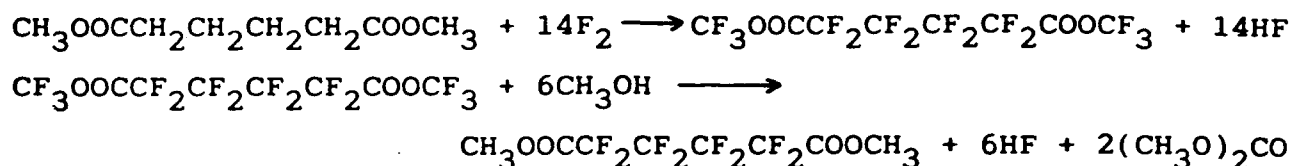
During the Phase I program, hexanediol diacetate was used to produce the dimethyl octafluoroadipate precursor for the octafluorohexanediol. Because of the Nylon chemistry, there are



more starting materials available for the C₆ diacid than for the C₅ diacid. One material investigated was caprolactone which should have reacted by the following scheme. This reaction was examined in some detail because problems were encountered during



the fluorination. After methanolysis, the best yields obtained were in the 40 to 50 percent range. The gas chromatogram showed some significant peaks that were quite close to the desired peak. We have noticed that ring systems can present rearrangement problems during fluorination, especially in larger than 6-membered rings. Although this is not always the case, we believe there is some internal rearrangement occurring in the caprolactone system. The gas chromatogram peak pattern does not indicate that there was a problem replacing all of the hydrogens. The amount of rearrangement could be controlled to some extent by changing the reaction conditions but a clean enough reaction was not obtained to make a practical process. The best starting material was found to be dimethyl adipate which reacts as follows. There is no steric problem replacing all of the hydrogens on the dimethyl adipate like that encountered with dimethyl glutarate. As a



result, the reaction can be run with somewhat higher flow rates and at lower temperature if desired. Dimethyl adipate was purchased from Morflex, Inc., Greensboron, North Carolina, for about 6 dollars per pound in 5-gallon quantities.

In a typical reaction, the reactor was loaded with about 6 gallons of Freon 113. The reactor temperature was kept between 15°C and 20°C. With a fluorine flow rate of 2.5 L/min and a nitrogen flow of 3.5 L/min (3 L/min mixed with F₂ and 0.5 L/min through the rotating seal), the dimethyl adipate was pumped in neat at a rate that maintained the oxygen reading at the exit of the alumina traps at between 1 and 2 percent. These conditions were maintained for 90 to 100 hours at which point the organic feed was stopped, the pump was rinsed with Freon 113, and the fluorine flow was reduced to 200 mL/min with a total nitrogen flow of 1 L/min. These conditions were held for 1 to 3 hours to insure that the material was perfluorinated. Then the fluorine flow was turned off, the reactor was purged and about a 20 percent excess of methanol was added to the reactor with the organic feed pump. The reactor was then dumped and the volatile components were removed in the metal still using the same procedure as described for the dimethyl hexafluoroglutarate. In a typical run, about 8 kg of starting material was used per run and about 12 kg of dimethyl octafluoroadipate was recovered. Yields ranged from 80 to 84 percent of crude product. This crude product was used directly in the reduction without further purification (distillation).

In the reduction, the general procedure outlined earlier was used with a 25 percent excess of sodium borohydride. The resulting diol tended to reflux in the sublimator when significant rates of sublimation were attempted. As a result, the product was distilled rather than sublimed. The apparatus used for the distillation consisted of a 12 L round bottom flask with an inverted U-shaped tube attached to it which acted as an air-cooled condenser. This tube was made of 25 mm glass tubing and had a fitting for a thermometer at the top. One end of the inverted U-tube was connected via a ground glass joint to the top of the 12 L round bottom flask and the other end was connected to a 2-neck 3 L flask via another ground glass joint. This 3 L round bottom flask was used as the distillation receiver. The other joint of the 3 L flask was fitted with a 12-inch length of 25 mm glass tubing coming out of it vertically. The top of this tube was connected to a two-stage vacuum pump protected by a liquid nitrogen trap. During the distillation, it was occasionally necessary to heat this 12-inch section of 25 mm tubing to melt condensed solid products and let them run back into the 3 L flask.

The main difficulty encountered in the distillation was due to the presence of water, isopropanol and sometimes acetone (used to wash the solids filtered off). These volatiles were held up for a long period of time during the distillation, causing bumping. Eventually it was found that refluxing the product under vacuum in the sublimator described earlier for a day or longer removed all of the volatile solvents. This makes the distillation of the product much easier because there is much less tendency of the material to bump.

A total of 80 pounds of 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol were produced. Of the three compounds made in volume during the Phase II effort, the octafluorohexanediol is the easiest material to produce. A ^{19}F NMR spectrum of a representative sample is shown in Figure 8.

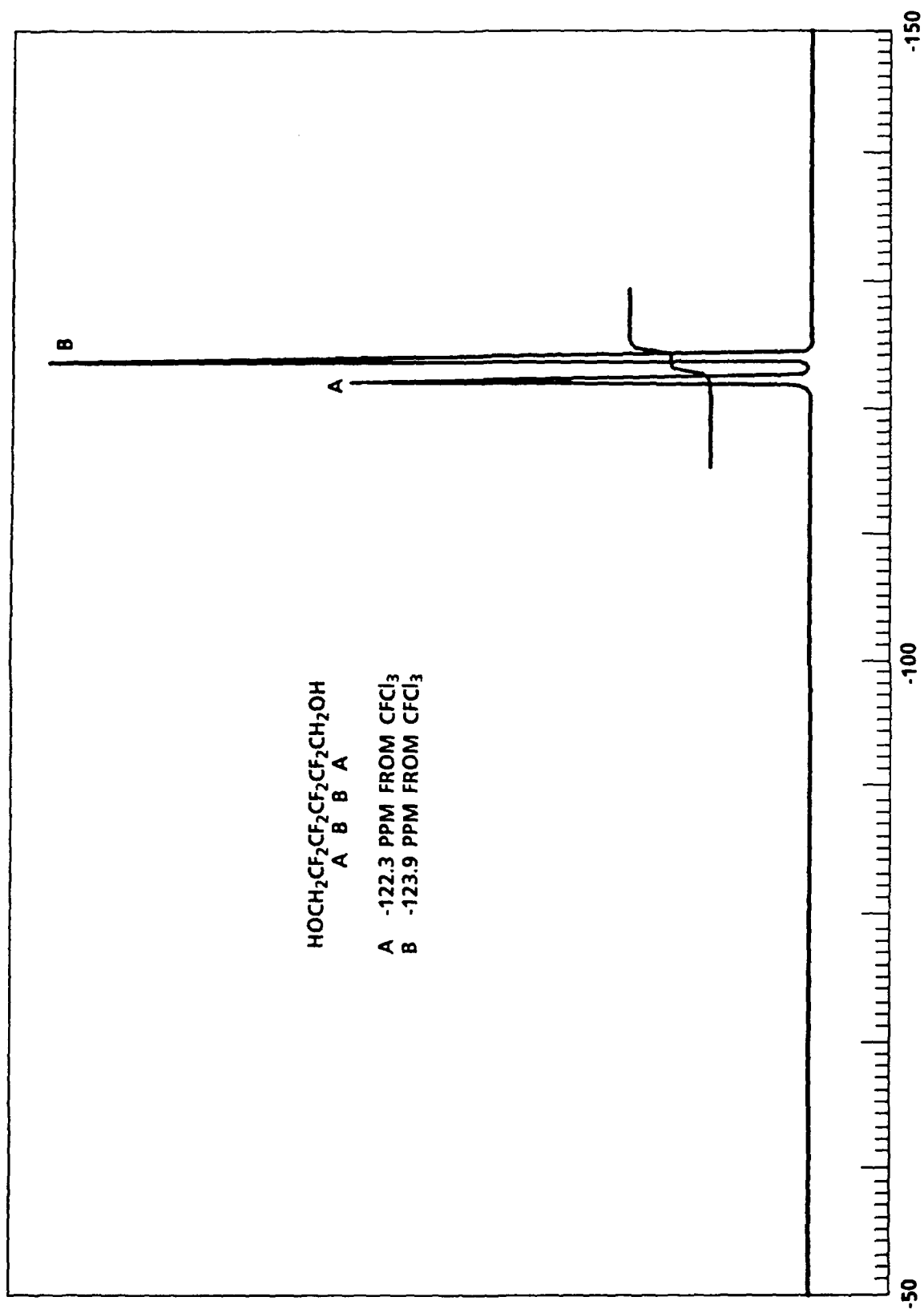


FIGURE 8. NMR SPECTRUM OF 2,2,3,3,4,4,5,5-OCTAFLUOROHXANE-1,1-DIOL

PRODUCTION OF 2,2,4,4,5,5,7,7-OCTAFLUORO-3,6-DIOXAOCANE-1,8-DIOL

The fluorination of ethers is more difficult than that of the preceding substrates because, during fluorination, ethers tend to form an acid-base complex with the by-product hydrogen fluoride that promotes fragmentation of the ether. One method of preventing this fragmentation is to fluorinate in the presence of sodium fluoride as outlined in U.S. Patent No. 4,755,567 issued to Exfluor Research Corp. However, for large scale fluorination of a simple system like triethylene glycol, this may not be the best method. Fluorination with a sodium fluoride slurry in the reactor adds several additional steps to the reaction. First, the addition of sodium fluoride reduces the capacity of the reactor. Second, there is a limit to the amount of sodium fluoride the reactor can be charge with and still have a stirrable slurry. As a result, the reactor could only produce about 3 kg of fluorinated product before the reaction would have to be terminated. Because the workup is labor intensive, the reduced batch size adds to the cost of the process. In addition, the reaction mixture must be filtered from the sodium bifluoride before the product can be distilled. The sodium bifluoride then must be heated in a nitrogen stream to regenerate sodium fluoride. All of these factors together result in a more expensive process. During the Phase II program, it was decided to try to eliminate the sodium fluoride from the reaction to see if an acceptable yield could be obtained. A somewhat lower yield may be acceptable if the process is simplified.

We used the same starting material that was used in Phase I, triethylene glycol diacetate. However, a less expensive method of making the diacetate than using acetyl chloride was desired. A good method appeared to be azeotropic distillation of water from a mixture of triethylene glycol, acetic acid, benzene, and an ion exchange resin. The first reaction worked quite well, so we continued to use this process. A small amount of free hydroxyl groups in the resulting product (as shown in the infrared spectrum, see Figure 9) was removed by treatment with a small amount of acetyl chloride. Unfortunately, subsequent batches of triethylene glycol diacetate were not analyzed as carefully before the product was fluorinated. Apparently, the ion exchange resin that was used tends to lose sulfuric acid which, when the products are filtered from the ion exchange resin, stays with the triethylene glycol diacetate. When this material was heated to

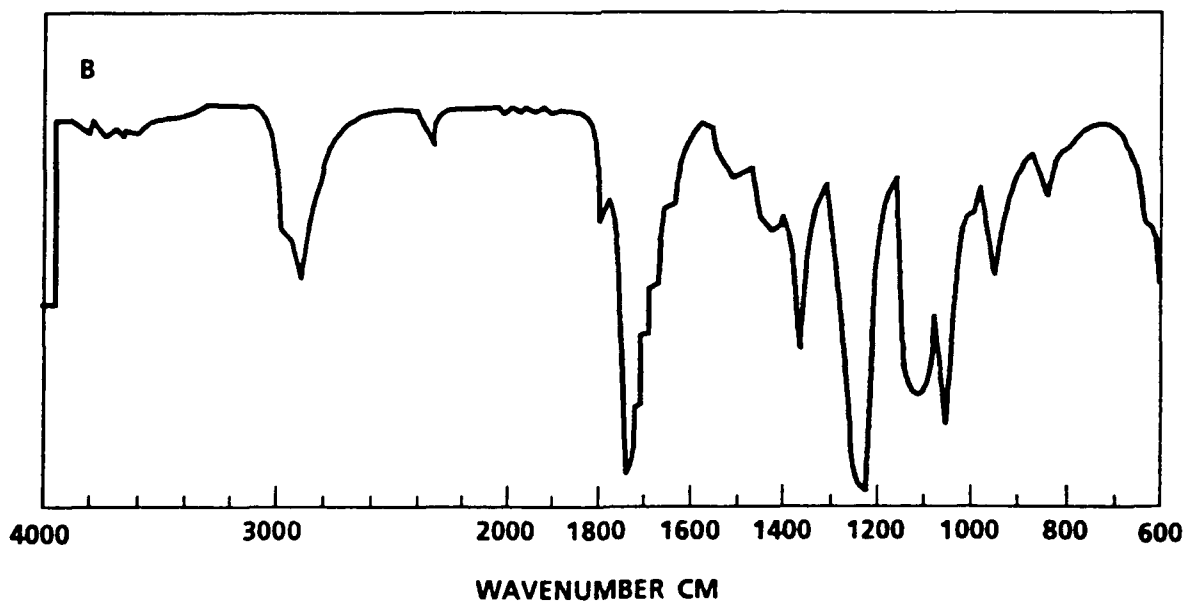
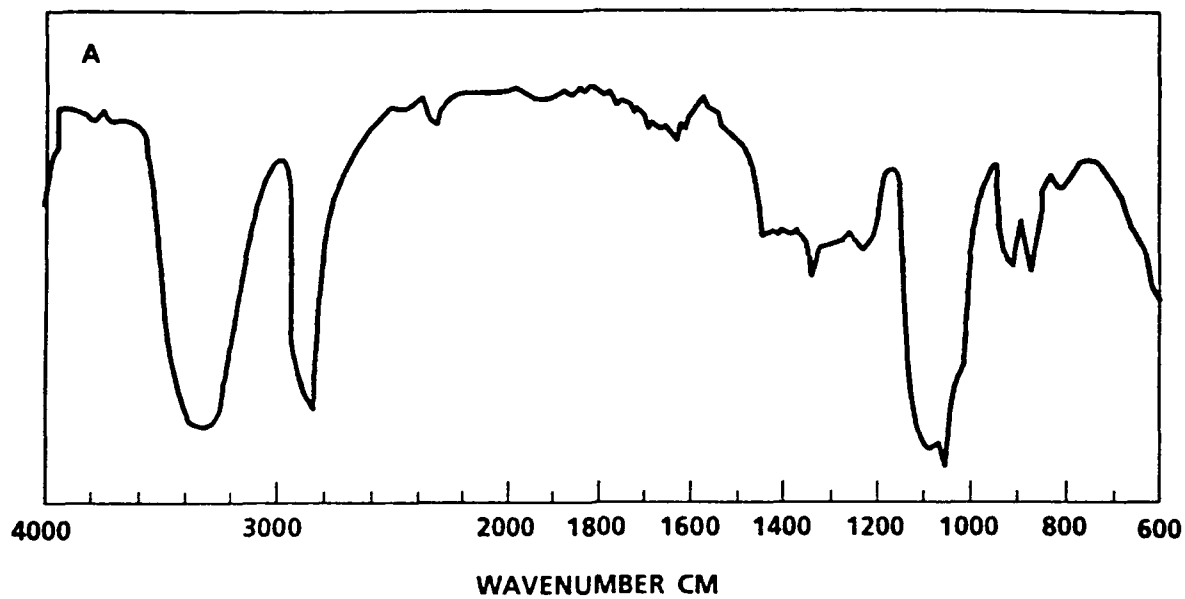


FIGURE 9. INFRARED SPECTOR OF (A) TRIETHYLENE GLYCOL AND
(B) TRIETHYLENE GLYCOL DIACETATE

remove benzene, acetic acid, etc., the triethylene glycol diacetate decomposed. This was the cause of the contamination of our early fluorination products with diethylene glycol products that were incorrectly attributed to fragmentation during the fluorination. The tendency of the ion exchange resin to lose sulfuric acid is apparently batch and temperature dependent and was much worse with a different ion exchange resin. Because of the impure starting material, much of the yield data obtained in the large reactor were meaningless. Some pure triethylene glycol diacetate was made with acetyl chloride. A series of optimization runs was done in a smaller reactor (about 1/4 the size of the large reactor) in order to get acceptable yields. A better method for producing triethylene glycol diacetate is to use para-toluenesulfonic acid as the catalyst.

In a typical reaction, 1265 g triethylene glycol (8.43 moles) and 1112 g acetic acid (18.5 moles) were placed in a round bottom flask. One gram para-toluenesulfonic acid was added along with 250 mL benzene. This mixture was stirred and refluxed while water was removed continuously using a water separator at the bottom of the condenser. Most of the water is collected in the first 3 hours, and after 6 hours the refluxing was stopped. Sodium bicarbonate powder was added to the cooled mixture which was then agitated and filtered. Benzene was removed under reduced pressure to give a crude product still showing some hydroxyl groups in the infrared spectrum. To this crude mixture, 65 mL of acetyl chloride was added at room temperature, the mixture was warmed to about 50°C for 3 hours, then nitrogen was bubbled through the mixture overnight. At this stage, the infrared spectrum showed no hydroxyl absorption and the gas chromatogram showed good purity. For best results this material was then mixed with sodium bicarbonate, shaken or stirred overnight, and filtered before use.

In the fluorination of triethylene glycol diacetate, hydrogen fluoride is removed from the reactor in two ways to minimize the decomposition caused by acid-base adduct formation with the starting material. The reactor temperature is raised, and the nitrogen flow is increased to minimize the amount of hydrogen fluoride present in the reactor at any given time. The best balance of conditions found are outlined below.

Eight gallons of Freon 113 were placed in the reactor. The fluorine flow rate was set at 2 L/min while the nitrogen flow was set at 9 L/min total (gas inlet and rotating seal purge). The reactor temperature was held at about 25°C. The oxygen reading at the exit of the aluminum oxide traps was maintained at about 0.7 percent while neat triethylene glycol diacetate was pumped into the reactor. These conditions are maintained for about 5 days. After this time, the organic feed pump is rinsed with Freon 113, the fluorine flow is reduced to 200 mL/min, and the nitrogen flow is reduced to about 1 to 2 L/min total. These conditions are maintained for about 30 to 60 minutes after which time the reactor is purged with nitrogen. An excess over the theoretical amount of

methanol (10%) is added to the reactor through the liquid inlet pump with the nitrogen flow set at about 2 to 3 L/min to remove the by-product hydrogen fluoride. In a typical reaction, about 8 kg of triethylene glycol diacetate is reacted and about 9 to 10 kg of product is recovered, after removing the solvent, methanol, and volatile by-products in the still at a still bottom temperature of up to 160°C. Typical yields range from 78 to 83 percent of theory. This product was used in the reduction without distillation. The product made from starting material that was contaminated with diethylene glycol diacetate required purification before reduction. Using a 10 plate Oldershaw column, the lower boiling diethylene glycol products were very slowly distilled off at atmospheric pressure in a glass systems over several days, until there was no evidence of the diethylene glycol product in the gas chromatogram of the distillation residue. This purification resulted in significant product losses as the boiling points of the fluorination products from diethylene glycol diacetate and triethylene glycol diacetate are quite close. The product purified in this manner was then reduced along with the product that was made with pure starting material.

In the reduction, the general procedure outlined earlier is used with a 25 percent excess of sodium borohydride. Ten moles (3500 g) of the dimethyl ester of 2,2,4,4,5,5,7,7-octafluoro-3,6-dioxaoctane-1,8-dioic acid were used in each reduction. The resulting diol was distilled as described for the octafluoro-hexanediol. At 0.01 Torr, the boiling point was between 100 and 105°C. The yield of diol in the reduction step after distillation was 92 percent. Some tars produced using either distilled or undistilled diacid starting materials remained as distillation residues. Fifty pounds of 2,2,4,4,5,5,7,7-octafluoro-3,6-dioxaoctane-1,8-diol were produced. A ¹⁹F NMR spectrum of a representative sample is shown in Figure 10.

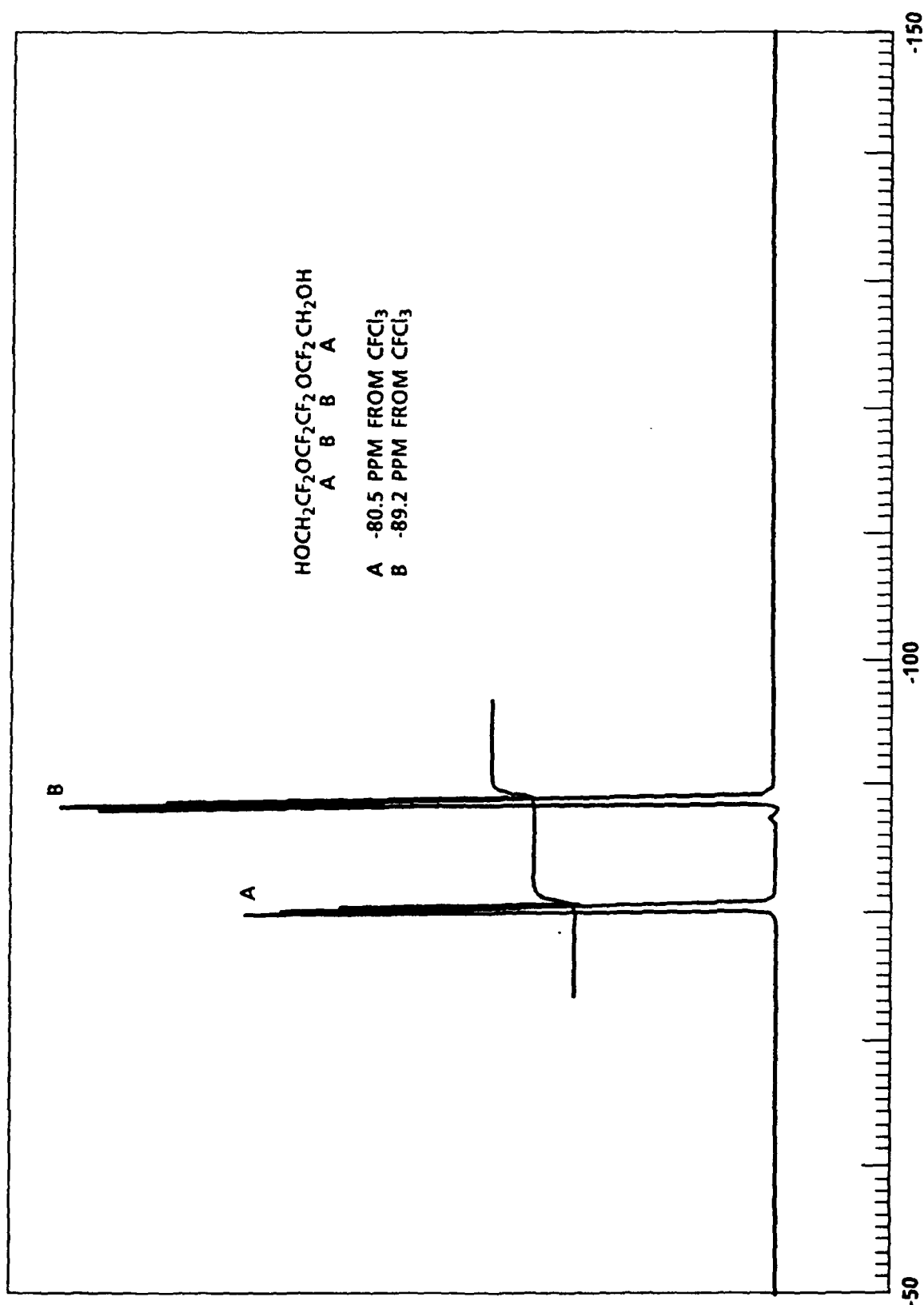
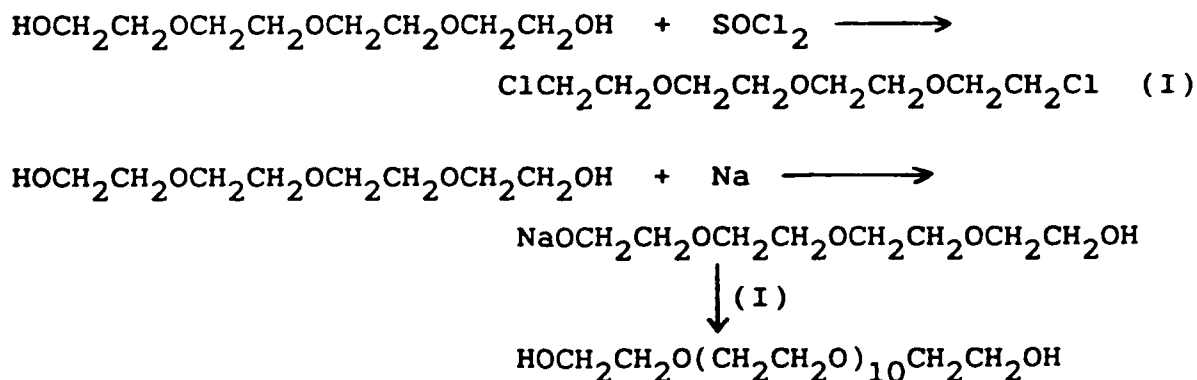


FIGURE 10. 19F NMR SPECTRUM OF 2,2,4,4,5,5,7,7-OCTAFLUORO-3,6-DIOXAOCANE-1,8-DIOL

PRODUCTION OF HIGH MOLECULAR WEIGHT PERFLUOROPOLYETHER DIOLS

An additional goal of this work was to produce small amounts of high molecular weight perfluoropolyether diols. To this end, diacetate esters of 600 MW and 1000 MW polyethylene glycols and of 650 MW and 1000 MW polytetramethylene glycols were fluorinated. A typical ^{19}F NMR spectrum of the product from 600 MW polyethylene glycol diacetate after treatment with methanol is shown in Figure 11. The first problem was to determine the amount of monofunctional by-product due to fragmentation during the fluorination. Fortunately, the Analytical Department of the 3M Company performed this analysis for us on a series of products made with different fluorination conditions. In general, we obtained a ratio of difunctional to monofunctional compounds of between 10 to 1 and 20 to 1. The polyethylene glycols were generally in the lower part of the range, and the polytetramethylene ether glycols were in the higher part of the range. Attempts to remove the monofunctional species by washing with solvents, distillation, and other methods were unsuccessful, primarily because all the commercially available polyethers have a broad molecular weight distribution. After a discussion of these results with NAVSWC personnel, it was decided to shift the emphasis to making a single component perfluoropolyether which would be exactly difunctional. Another factor was that the mixtures of broad molecular weight range could not be separated by distillation from tars produced in the reduction step.

Our first attempt to make a single component polyether was to produce dodecaglyme by the Williamson synthesis outlined below.



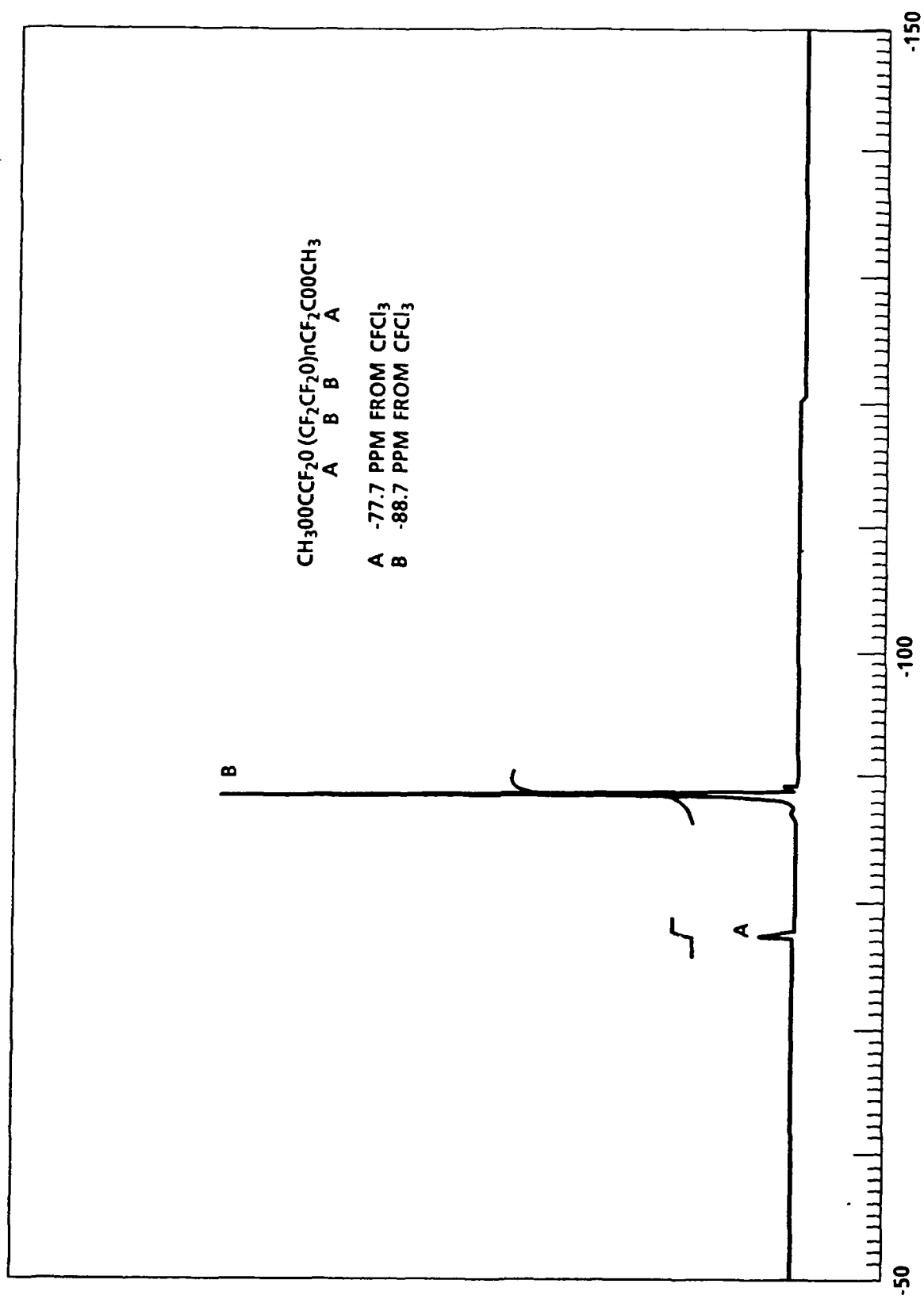


FIGURE 11. ¹⁹F NMR SPECTRUM OF THE REACTION PRODUCT PREPARED FROM THE FLUORINATION OF 600 MW POLYETHYLENE GLYCOL (ACETYLATED) FOLLOWED BY METHANOLYSIS

Although Williamson syntheses normally give rather low yields, and the product could not be distilled, it was decided to fluorinate the crude product and see if the product could be purified by distillation after the fluorination. These efforts were not successful in giving a pure enough product.

We succeeded in carefully distilling a mixture of polytetramethylene ether glycols to isolate a tetramer in reasonable purity (95 percent). This tetramer was acetylated with acetyl chloride and fluorinated at 25°C using conditions similar to those used with triethylene glycol diacetate. After treatment with methanol, the product was distilled under vacuum of about 0.01 Torr using a 10-plate Oldershaw column to give a very pure product that distilled at 122°C. The overall yield after distillation was about 70 percent of theory. The product contained only a trace of trimer. Most of the yield losses were due to product holdup in the still and carry over with the forerun. Obtained from 834 g of diacetate was 1200 g of distilled product.

The reduction of this material turned out to be much more difficult than anticipated. The first attempt used the general reduction procedure with a two-fold excess of sodium borohydride. When about 1/3 of the diacid ester was in the reactor, a very sticky mass separated from the solution and began adhering to the reactor walls, stirrer blades, etc. The reaction was stopped at this point to find a solvent that would dissolve the sticky mass. Addition of water to the isopropanol redissolved the product while normal laboratory solvents did not seem to work very well. A second reduction was therefore attempted in which 626 g of starting material were added from a dropping funnel to a mixture of 60 g of sodium borohydride, 1 L of isopropanol, and 100 mL of water in a 3 L 3-neck flask. Because the starting material was not very soluble in this solvent mixture in the cold, the dimethyl ester of the diacid was added at a rate sufficient to keep the temperature at about 30°C. After all of the starting material was added (about 90 minutes), the flask was heated to 60°C and held at this temperature for about 90 minutes. During this period, the product started to separate and stop the stirrer. Another 70 mL of water had to be added to permit stirring to continue. The flask was then cooled and 300 mL of a saturated solution of ammonium chloride in water was added slowly. The reaction mixture once again reached a sticky stage and stirring was erratic until all of the ammonium chloride was added. After sitting overnight, the mixture was filtered and the isopropanol and water were removed by distillation. The crude product showed a single peak in the gas chromatogram. This material was then distilled under a hard vacuum (0.01 Torr) to give 455 g of crude product (78 percent yield). There was much more tar formed and carried over in the distillation than normal, and the tars were high melting and hard. The crude product was redistilled at 0.01 Torr to give

a material that distilled at about 120°C. The gas chromatogram and ^{19}F NMR spectrum of this material look very good, but the product appearance is not too good. The product appears to be a cloudy, viscous liquid. The ^{19}F NMR spectrum of the product before redistillation is shown in Figure 12. We are not very happy with the reduction step for this material but no further work could be done due to lack of starting material. A total of 433 g of the redistilled product were produced. The product name is 2,2,3,3,4,4,6,6,7,7,8,8,9,9,11,11,12,12,13,13,14,14,16,16,-17,17,18,18-octacosafuoro-5,10,15-trioxanonadecane-1,19-diol ($\text{HOCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{CH}_2\text{OH}$).

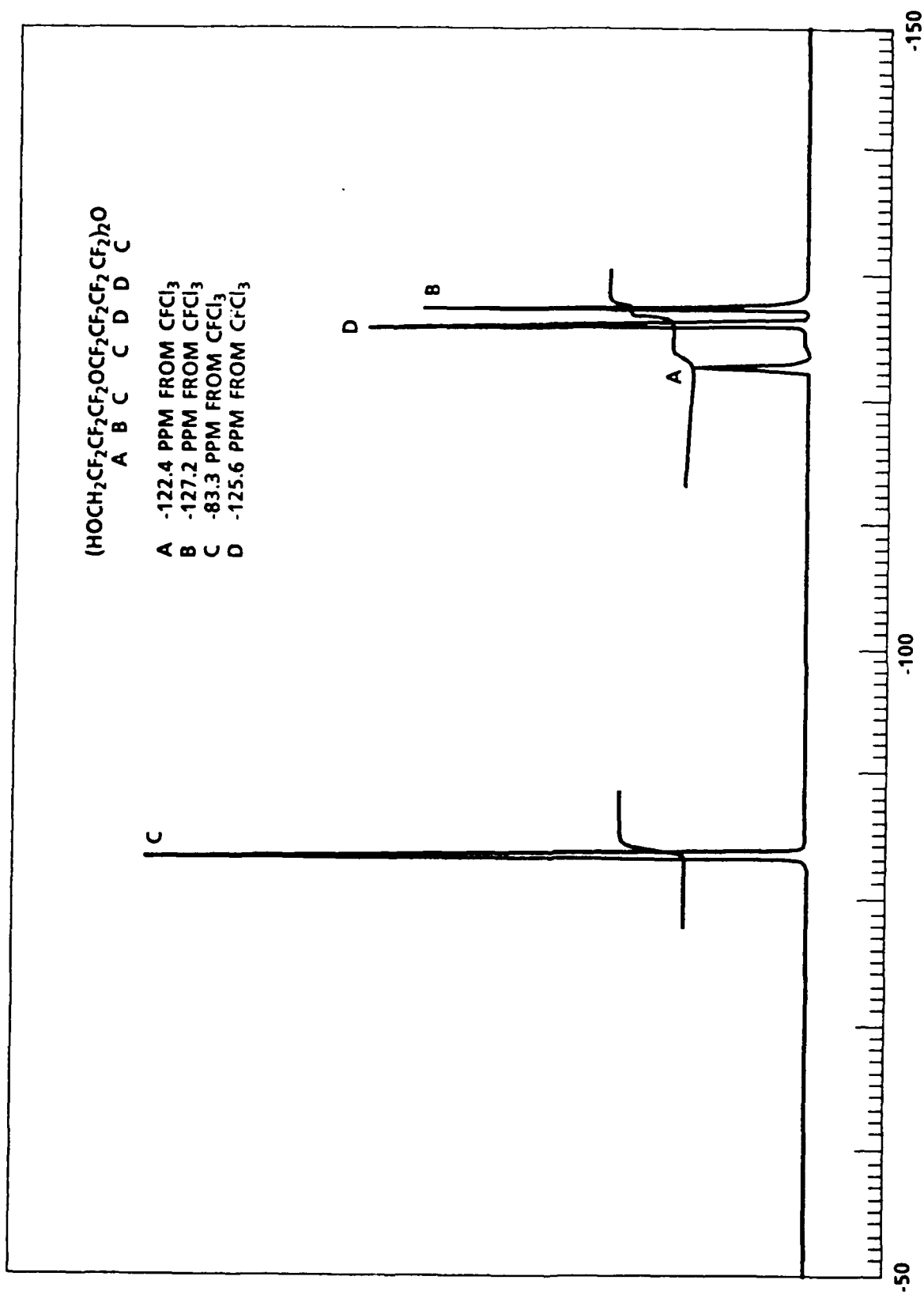


FIGURE 12. ¹⁹F NMR SPECTRUM OF 2,2,3,3,4,4,6,6,7,7,8,8,9,9,11,11,12,12,13,13,14,14,16,16,17,17,18,18-OCTACOSAFLUORO-5,10,15-TRIOXANONADECANE-1,19-DIOL.

DISCUSSION

Of the three major diols synthesized, octafluorohexanediol is by far the easiest to produce. At this time, however, only about 57 percent of the fluorine used is contained in the final product because the methyl groups of the dimethyl adipate consume fluorine but are not useful products. It may be possible to get this number closer to 80 percent by changing the starting material to a polyester made from adipic acid and hexanediol. The optimum molecular weight of the polyester and other factors need to be determined, but we believe this approach will improve the fluorination efficiency with further work. The use of a polyester would also allow separation of the solvent from the product by distillation before methanolysis. This would reduce the solvent losses and allow solvent recycling without any treatment other than distillation. A similar approach should work for the preparation of hexafluoropentanediol.

The other main problem with the process at this time is that Freon 113 is used as the solvent. Freon 113 solidifies at -35°C where it still has a significant vapor pressure. As a result, some of it is entrained with the nitrogen during the fluorination. This problem may be solved by recycling the nitrogen gas using a design like that shown in Figure 13. In this system, most of the exiting nitrogen is mixed with the inlet gas and fed back into the reactor. Only a small amount of gases exit through the condenser. This was tried on a small scale using a Teflon diaphragm pump to recirculate the nitrogen. By inserting a bed of sodium fluoride pellets into the gas recirculation loop, the by-product hydrogen fluoride can be removed. This method worked very well, and on a small scale, the solvent losses were cut to about one pound for every five pounds of product. Even better results may be obtained on a large scale or if a much colder condenser is used. We still use some fresh nitrogen gas in the inlet and for the rotating seal, so the system is not completely closed. However, the flow of gases through the condenser is substantially reduced and it may be possible to freeze out the Freon 113 with a second much colder condenser that is either changed or warmed periodically to prevent it from plugging.

Alternative solvents are also a possibility, although most are more expensive at this time. Without gas recirculation or colder condensers, we lose about 1 pound of solvent for every

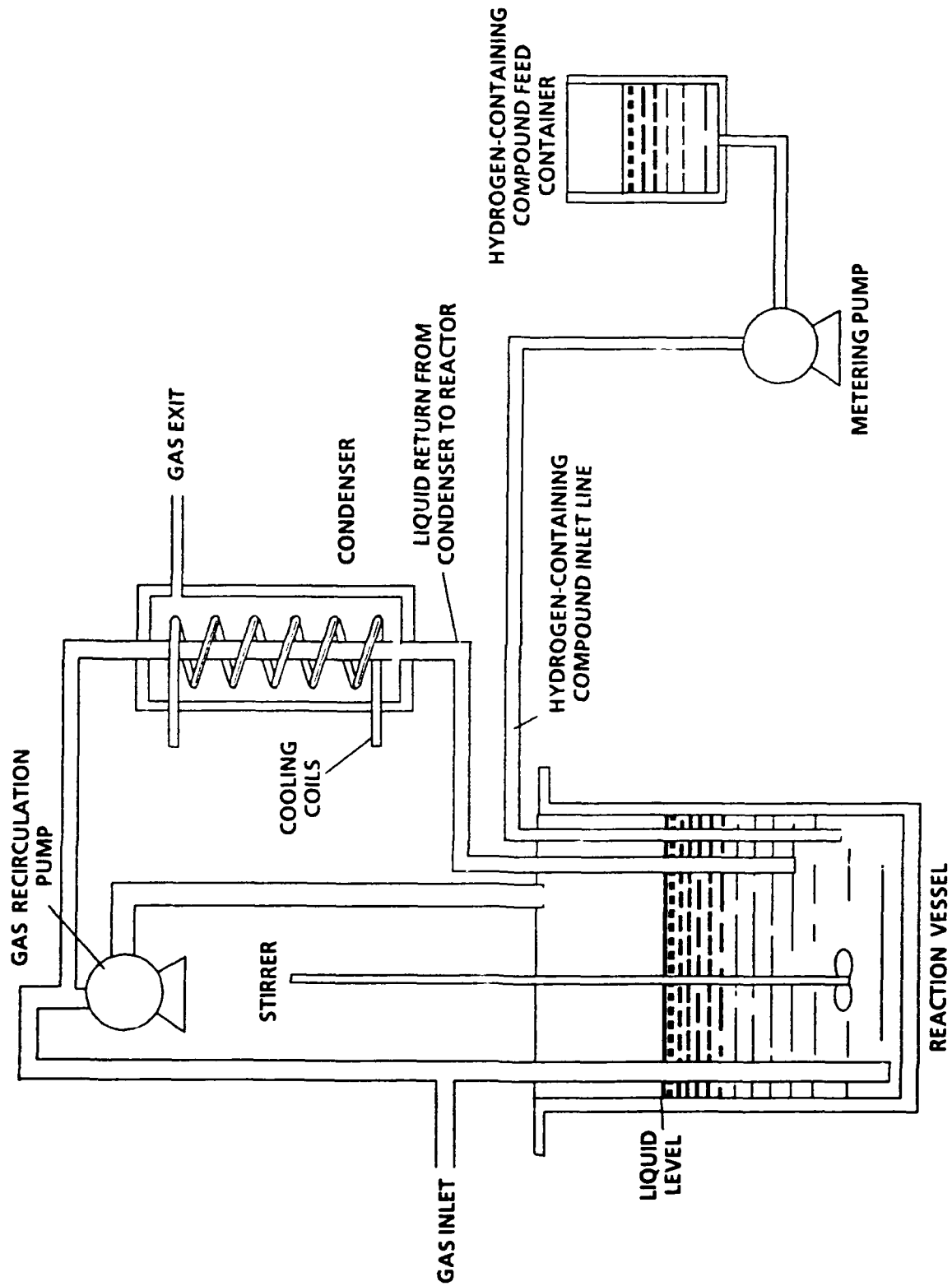


FIGURE 13. SCHEMATIC DRAWING OF FLUORINATION REACTOR WITH A GAS RECIRCULATION SYSTEM

pound of diacid not containing ether linkages, and several pounds for the ether-containing diacids which require a higher nitrogen purge rate. On the small scale, on which we are currently operating, this is not a major problem. The future availability of Freon 113 is, however, in question. We are working on alternative solvents that do not present these problems.

By far the most expensive part of producing the fluorinated diols is fluorine gas. For the present Phase II work, fluorine was purchased in cylinders at a cost of about \$45 per pound. In the next 6 to 9 months, we hope to start operating a small fluorine cell (1000 to 2000 amps). Hydrogen fluoride in cylinders costs 6 to 10 dollars a pound (or 60 cents a pound in tank cars). With this starting material, we hope to produce fluorine on a small scale for 10 to 15 dollars a pound. Even with additional improvements in fluorine efficiency by selecting different starting materials, it is not likely, however, that fluorinated diols will become low cost fluorocarbons. Their synthesis still involves a multi-step process using fairly expensive materials such as fluorine and sodium borohydride. Of the three materials we made in significant quantities during this program, octafluoro-triethylene glycol is the most expensive and octafluorohexanediol should be the cheapest to produce.

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